# ENVIRONMENTAL PROTECTION

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## POROUS CERAMIC MEMBRANES FOR REGENERATION OF WASTE SULFATE SOLUTIONS

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The parameters of immersed ceramic membranes used in the recovery of iron powder by electrolysis of the waste pickling sulfate solution are considered. Mathematical models of the main parameters of the porous ceramic membranes are specified, and the results of their use in electrolysis are described.

Technologies offering solutions to environmental problems are of special interest lately, and the methods for recovering metallic powder from metallurgical waste continue to be topical. The method for utilization of pickling sulfate solutions (PSS) by electrolysis using insoluble lead anodes and a channeled vibrating cathode (USSR Inventor's Certif. No. 219301) makes it possible to regenerate sulfuric acid on the anode and obtain iron powder without additional use of a metal-containing material. The application of this method significantly diminishes the discharge of toxic waste into the ambient environment. The electrolysis of waste PSS is carried out with a separation of the space between the electrodes, which excludes mixing of the regenerated acid with the initial electrolyte.

The membranes used to separate the bath space in electrolysis should have high chemical resistance, low specific resistance in an electrolyte, should prevent mixing of the solutions, and have high porosity and sufficient strength [1]. The width of the membrane should not exceed 3 mm, which is recommended taking into account the technological possibilities of making relatively large-sized articles and the need to reduce the electrical resistance.

The water permeability coefficient of the membrane should not exceed $4.3 \times 10^{-12}$ m$^2$/(sec · Pa) [1], since the lower the permeability, the lower the losses of the electrolysis products. The mean pore radius should be 0.8 – 1.0 μm [1, 2]. This prevents convection transfer and retards the diffusion of the electrolysis products. However, a decrease in permeability can be accomplished not only by a small size of pores, but also by a low through porosity, which leads to increased resistance and a decreased yield of the electrolysis products along the current. A decrease in through porosity is undesirable for immersed partitioning membranes.

Membranes can be made of porous ceramics, asbestos, dense tissues, sintered glass, porous plastics, etc. [1].

For regeneration of waste PSS it is advisable to use immersed partition membranes made of porous ceramics. Ceramic membranes satisfy all requirements, are easy to manufacture, and have a low production cost. The conditions of electrolysis do not require any flows via the membranes inside the bath or selective passage of ions. Despite the fact that partitioning membranes are needed in various hydrometallurgical processes, the contemporary literature pays little attention to the formulas and methods for making such membranes. The industrial production of dividing membranes for electrolysis is currently insignificant. The purpose of the present study is to develop a method for their production and to analyze the obtained results.

The experiment was based on ceramic mixtures consisting of Vladimirskii quarry clay (the bulk of the mixture), chamotte, graphite (the burning-out additive to develop a porous structure), and a glass binder additive.

To determine the optimum composition of the ceramic mixture, a four-factor experiment was carried out in accordance with the matrix of the rotating-table central composition plan $2^4$. The variable parameters in the experiments were the contents of glass $C_{gl}$, chamotte $C_{ch}$, and graphite $C_{gr}$ and the milling duration in a SAND-1 planetary ball mill. The following output parameters describing the main properties of the membranes were chosen for optimization: modification of linear dimensions (shrinkage), %; total porosity, %; the water permeability coefficient $W$, m$^2$/(sec · Pa); the specific resistance in electrolyte $\rho$, $\Omega \cdot$ m, the average pore radius $r_{av}$, μm; and the bending strength $\sigma_b$, MPa.

The samples were produced by casting in gypsum molds, then dried and fired (sintered) at a temperature of 1000°C.

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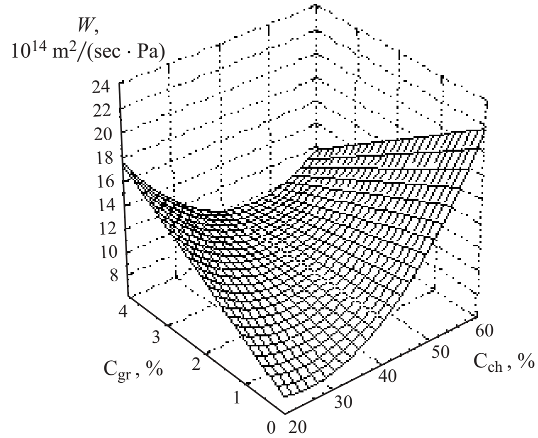


**Fig. 1.** Water permeability coefficient of ceramic membranes, $W \times 10^{14} = f(C_{ch}, C_{gr})$.

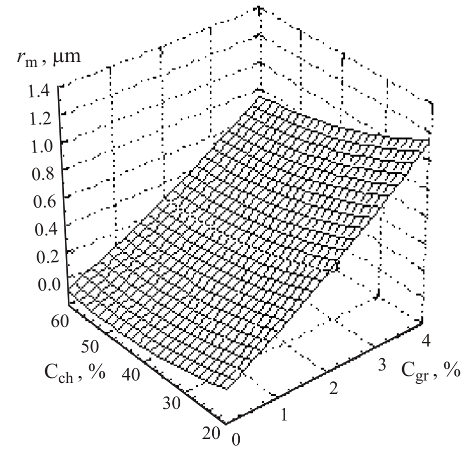


**Fig. 3.** Average pore radius depending on the variable factors, $r_{av} = f(C_{ch}, C_{gr})$ at τ = 35 min.

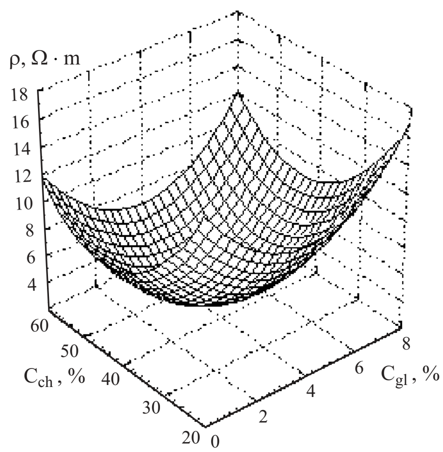


**Fig. 2.** Specific resistance of membranes in electrolyte, $\rho = f(C_{ch}, C_{gl})$, $C_{gr} = 2\%$, τ = 35 min.

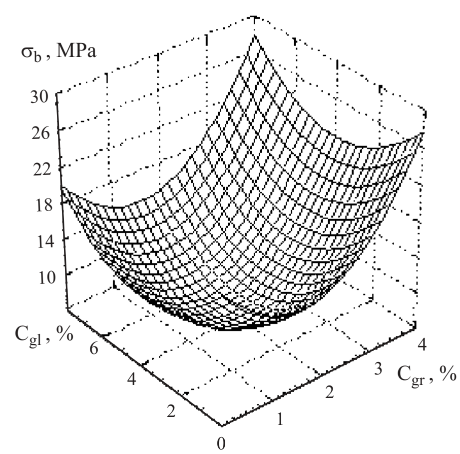


**Fig. 4.** Bending strength of the membrane material $\sigma_b = f(C_{gl}, C_{gr})$ at τ = 35 min.

A mathematical model describing the significance of the contribution of the considered factors was obtained for the water permeability coefficient:

$$W \times 10^{14} = 14.99 + 0.012C_{ch}^2 - 0.606C_{ch} - 0.127C_{ch}C_{gr} + 5.08C_{gr}.$$

It follows from this model that the content of chamotte and graphite in the membrane material has the highest impact on permeability. These components are introduced to develop a system of through pores allowing for the passage of the electric current. An increase in the amount of the specified components in the membrane material increases its porosity and, consequently, the permeability of the membrane (Fig. 1).

The specific electric resistance of ceramic membranes immersed in an electrolyte is described by the model (Fig. 2):

$$\rho = 43.256 - 1.216C_{ch} - 0.229\tau - 2.66C_{gl} - 4.64C_{gr} + 0.333C_{gl}^2 + 0.137C_{ch}^2 + 1.16C_{gr}^2 + 4.16 \times 10^{-3}\tau^2.$$

The average pore radius depending on the variable factors is described by the mathematical model:

$$r_{av} = 0.353 + 0.258C_{gr} + 0.0125C_{gr}^2 - 1.67 \times 10^{-3}C_{ch}C_{gr} - 0.0186C_{ch} + 1.9 \times 10^{-4}C_{ch}^2 - 3.05 \times 10^{-3}\tau + 4.35 \times 10^{-5}\tau^2.$$

The model obtained for the mean pore radius indicates that the quantity of graphite introduced into a ceramic mixture has the highest effect on this parameters (Fig. 3). The graphite is uniformly distributed in the volume, and when in firing it burns out in a small amount, it forms the pores, whose size is insufficient for accomplishing the set purpose. An increase in the graphite content leads to the formation of aggregates, and their burning out in firing allows for the formation of pores of the required diameter.

The chamotte content in the membrane material does not have a significant effect on the size of the emerging pores.

Based on the sample testing results, a mathematical model describing the bending strength of the membrane material was obtained (Fig. 4):

$$\sigma_b = 29.02 - 7.29C_{gr} - 0.67\tau + 3.08C_{gr}^2 + 0.385C_{gl}^2 + 0.012\tau^2.$$

The lowest strength values are observed within the range correlating with a high porosity and a low specific resistance, which ensure efficient performance of the membrane. A comparison of the strength values obtained in the experiment with the data quoted in the literature indicates that even the minimum strength value satisfies the requirements imposed on the membranes and exceeds the values specified in [1] by an order of magnitude.

A porous ceramic material for partition membranes with the following properties was obtained: total porosity 55%, water permeability coefficient $1.55 \times 10^{-12}$ m$^2$/(sec · Pa), specific resistance in an electrolyte 1.79 Ω · m, average pore radius 0.77 μm, and bending strength 5 MPa. The modification of the linear dimensions (shrinkage) in producing membranes was equal to 8.2%.

The use of ceramic membranes for dividing the space between the electrodes in the electrolysis of waste PSS makes it possible to preserve the yield of iron powder at a level of 65 – 70%, to remove the sulfuric acid regenerating in the anode space, and to return it to the pickling site. The content of acid regenerated in 3 h of electrolysis grows from 0.1 to 1.0% (waste solution) to 3.0%. The initial pickling solution is 15% $H_2SO_4$. The full regeneration of a waste pickling bath depending on the density of the current passing via the bath and the quantity of extracted iron can last 15 – 24 h, which satisfies the pickling conditions.

The proposed method can be used at enterprises with small pickling sites for rolled product (1 – 2 baths per day).

## REFERENCES

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